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Local Motion of Polystyrene Chain Studied by the Fluorescence Depolarization Method

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The local motion of polystyrene chains in dilute solutions was studied by measuring the photostationary and time-resolved fluorescence depolarization of the perylene probe introduced in the polystyrene chains. The fluorescent probes were introduced either randomly in the interior of the chain or at the chain ends and the relaxation time of the local motion of polystyrene chains was analyzed. The time-resolved anisotropy ratio was represented roughly by a single exponential decay either in the interior of the chain or at the terminal position. The relaxation time in the interior of the chain is twice as large as that at the ends. Effects of molecular weight and solvent on the relaxation time were also studied.

KEY WORDS: Local Motion/ Polystyrene/ Fluorescence Depolarization
Method/ Perylene/ Dilute Solution/

INTRODUCTION

Investigation of the dynamic properties of polymer chains is important to understand the macroscopic behavior of polymers. Recently there have been extensive investigations on the dynamic behavior of polymer chains in dilute solutions.¹⁻⁴⁾ The fluorescence depolarization method is a direct method for studying the motional relaxation process of polymer chains.⁵⁻⁹⁾ This method can be applied for steady-state measurement and time-resolved measurement. A recent development of electronics makes the latter advanced and the time-resolved measurement in the nanosecond and subnanosecond time region enables us to observe directly the orientation autocorrelation function of the transition vector. Valeur and Monnerie¹⁰⁾ investigated the local motion of anthracene-labeled polystyrene in dilute solutions by the time-resolved method. Recently, Viovy et al.¹¹⁾ reinvestigated the local motion of anthracene-labeled polystyrene and tested various theoretical models. We applied the steady state method to various flexible polymer chains, e.g., polyacrylamide,^{12,13)} polyethyleneimine¹⁴⁾ and showed that the average relaxation time of the terminal segment motion of these polymers lies in the region between 1 to 19 ns in ordinary solvents. Very recently, we studied the local chain dynamics of anthracene-labeled poly(methyl methacrylate) by the time-resolved measurement and discussed the dynamic behavior of the polymer chains in dilute solution on the basis of theoretical models¹⁵⁾.

In this investigation, we measured the relaxation time of polystyrene chain by the time-resolved measurement as well as by the photostationary measurement of fluorescence depolarization and tried to elucidate the dynamic behavior of local motion of the polystyrene chain in dilute solutions.

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EXPERIMENTAL

Preparation of Polystyrene Incorporating Perylene Probe. Two series of polystyrene samples coded Pst A and Pst B were prepared. For the Pst A series the probe was introduced randomly in the polymer chain, while for the Pst B series the probe was attached at the terminal segments, as shown schematically in Fig. 1.

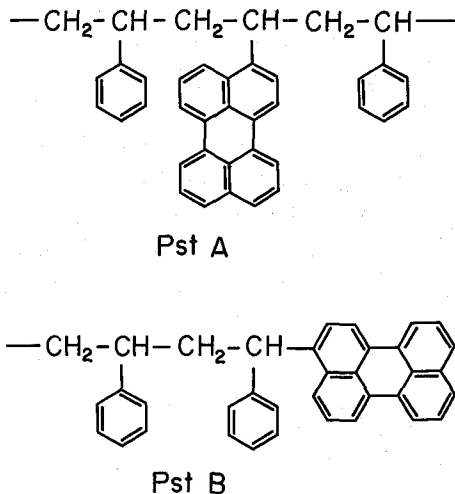


Fig. 1. Labeled polystyrene samples.

3-Vinylperylene and 3-bromoperylene were prepared to introduce perylene to a polymer chain. 3-Vinylperylene was synthesized by the Wittig reaction of 3-formylperylene which was obtained by Vilsmeier's reaction of perylene. 3-Bromoperylene was synthesized by bromination of perylene with cupric bromide in azeotropic mixtures of benzene and ethanol.¹⁶⁾

Pst A series was obtained by cationic copolymerization of styrene and a trace amount of 3-vinylperylene with BF_3OEt_2 in ethylene dichloride. Styrene was purified by the usual method and distilled over CaH_2 under reduced pressure. Ethylene dichloride was purified by the usual method and distilled over P_2O_5 . BF_3OEt_2 was distilled before use. Styrene, 44 mM, and 3-vinylperylene, 3.6 μM , in 255 ml of ethylene dichloride were polymerized with an addition of ca. 1 mmol of BF_3OEt_2 under a nitrogen atmosphere at 0°C . The reaction was allowed to continue for 4.5 h. Then the reaction was terminated with a small amount of methanol. The polymer was purified by precipitation from benzene solution to methanol. The process was repeated several times to eliminate unreacted vinylperylene. The polymer was fractionated into six fractions by successive precipitation with methanol from the benzene solution. The first, third and fifth fractions coded Pst A1, Pst A2 and Pst A3 were used for the measurements.

Pst B series was obtained by living polymerization of styrene initiated by butyllithium in THF solution. The monofunctional living end of this polystyrene was

coupled with 3-bromoperylene. The coupling reaction was continued for one day. Then a small amount of methanol was added to the reaction mixture to kill the unreacted living end. This polymer was purified by the same method described for Pst A series.

Characterization of the Samples. Table I shows the molecular weights and perylene contents of the samples. M_n and M_w of the samples except for Pst B3 were determined using gel permeation chromatography which was calibrated with standard polystyrene samples. The value M_n of Pst B3 was obtained by vapor pressure osmometry. Perylene content per gram of polystyrene was determined from the absorbance at the maximum of the absorption spectrum of a sample containing a certain weight of polystyrene, assuming that the extinction coefficient at the maximum (435 nm) is $3.95 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.¹⁷⁾ The number of perylene per polymer molecule is much less than 1 for all samples. Therefore, the depolarization caused by intramolecular energy migration is considered to be negligibly small. Judging from the reaction mechanism, the perylene probe is located randomly in the interior of the polystyrene chain in the Pst A series and the perylene residue is located at the end of the polymer chain in the Pst B series.

Table I. Characterization of Perylene Labeled Samples

Sample	M_n $\times 10^{-4}$	M_w/M_n	Perylene per gram of sample ($\mu\text{mol/g}$)	Perylene number per polymer molecule
Pst A1	5.0	2.0	0.4	0.02
Pst A2	2.8	1.3	0.5	0.01
Pst A3	1.2	1.4	0.4	0.005
Pst B1	6.5	1.2	0.3	0.02
Pst B2	1.7	1.3	3.6	0.06
Pst B3	0.24	—	3.8	0.009

Absorption and Fluorescence Spectra. Fig. 2 shows the absorption and fluorescence spectra of the samples. The spectra are similar to that of perylene but the maxima of the spectra are displaced to the red by 21 and 14 nm compared with that of perylene for Pst A1 and for Pst B1, respectively.

Measurement of Lifetimes and Anisotropy Ratios.

Apparatus: Anisotropy ratio of fluorescence was determined by the photostationary measurement and by the time-resolved measurement.

For a photostationary measurement we used a light scattering photometer (Shimadzu DI-10) equipped with a Glan-Thompson prism as a polarizer and a Polaroid dichroic filter as an analyzer. A mercury line of 436 nm was used for exciting the perylene chromophore and the fluorescence was measured through a suitable filter to cut off the exciting light. Temperature of the solution was controlled by a thermostat jacket. The polarized axis of exciting light was set to be normal to the plane of the

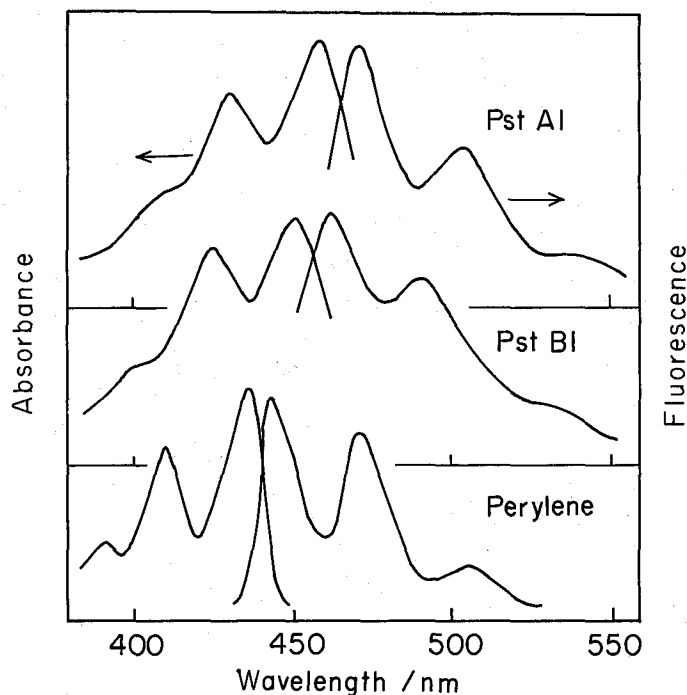


Fig. 2. Absorption and emission spectra of Pst A1, Pst B1 and perylene in THF.

optical system. Two polarized components of the fluorescence, I_{\parallel} and I_{\perp} were measured at right angle to the incident light by rotating the analyzer. The apparatus was calibrated so that the intensities of the two polarized components were identical when the axis of the polarizer was set to be in the plane of the optical system.

A single photon counting technique was used to measure the excited singlet lifetimes and the time-resolved anisotropy ratios.¹⁸⁾ The apparatus consists mainly of an Ortec nanosecond fluorescence spectrometer (a nanosecond pulser (Ortec 9352), a single photon counting phototube (RCA 8850), a time-to-pulse height converter (Ortec 457), and a multi-channel analyzer (Hitachi 505)). The optical system was similar to that for the photostationary measurement.

Procedures for Lifetime Measurement: The total fluorescence intensity, $f(t)$ is expressed by eq. (1) where $f_{\parallel}(t)$ and $f_{\perp}(t)$ are parallel and perpendicular components when a sample is excited by linearly polarized light.

$$f(t) = f_{\parallel}(t) + 2f_{\perp}(t) \quad (1)$$

If the overall time function of the exciting pulse and the detector is denoted by $P(t)$ and the fluorescence response function is shown by $F(t)$, then the observed fluorescence response, $f(t)$ is given by eq. (2).

$$f(t) = \int_0^t P(t') F(t-t') dt' \quad (2)$$

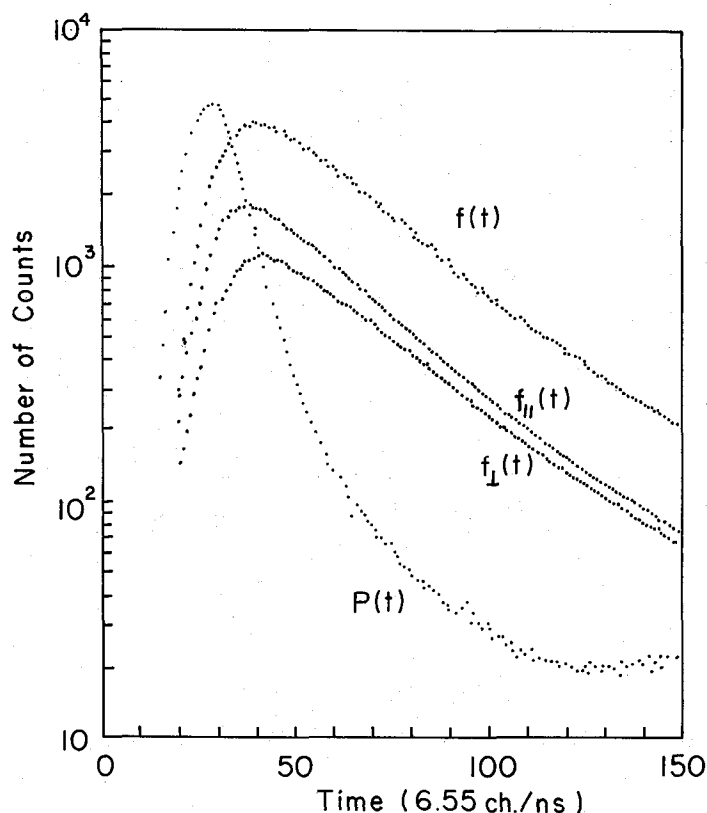


Fig. 3. Shapes of the exciting light pulse $P(t)$, total fluorescence intensity $f(t)$ and its components, $f_{||}(t)$ and $f_{\perp}(t)$ for Pst A1 in cyclohexanone..

In practice, $P(t)$ was measured directly and $f(t)$ was simulated by using a trial function $F(t)$. In the present study the most appropriate function of $F(t)$ was found to be a single exponential decay. Fig. 3 shows an example of $P(t)$ and $f(t)$ for Pst A1 in cyclohexanone. The lifetime of the sample was 4.2 ns.

Procedures for Anisotropy Ratio $r(t)$ Measurement: Parallel and perpendicular components of polarized fluorescence intensity to the exciting polarized light $f_{||}(t)$ and $f_{\perp}(t)$ are expressed with the response functions, $i_{||}(t)$ and $i_{\perp}(t)$, and $P(t)$ as shown in eq. (3).

$$f_{||}(t) = \int_0^t P(t') i_{||}(t-t') dt'$$

$$f_{\perp}(t) = \int_0^t P(t') i_{\perp}(t-t') dt' \quad (3)$$

As an example the observed curves $f_{||}(t)$, $f_{\perp}(t)$ for Pst A1 in cyclohexanone solution are also plotted in Fig. 3. These plots are well fitted to the simulation curve made by substituting eq. (4) into eq. (3) where the lifetime $\tau=4.2$ ns is used. Eq. (4) is based on the assumption that the system has only one relaxation time ρ .¹⁰⁾

$$\begin{aligned} i_{\parallel}(t) &\propto (1 + 2\exp(-3t/\rho)r_0)\exp(-t/4.2) \\ i_{\perp}(t) &\propto (1 - \exp(-3t/\rho)r_0)\exp(-t/4.2) \end{aligned} \quad (4)$$

The relaxation time ρ obtained in this manner agrees with the one obtained by the steady state measurement (see eq. (5)).

RESULTS AND DISCUSSION

Non-Steady State Measurements of Rotational Relaxation Time. Figs. 4 and 5 show the plots of $r(t)$ against time for Pst A1 and Pst B1 in cyclohexanone. They were calculated from the polarization components and simulated by setting r_0 as a parameter.

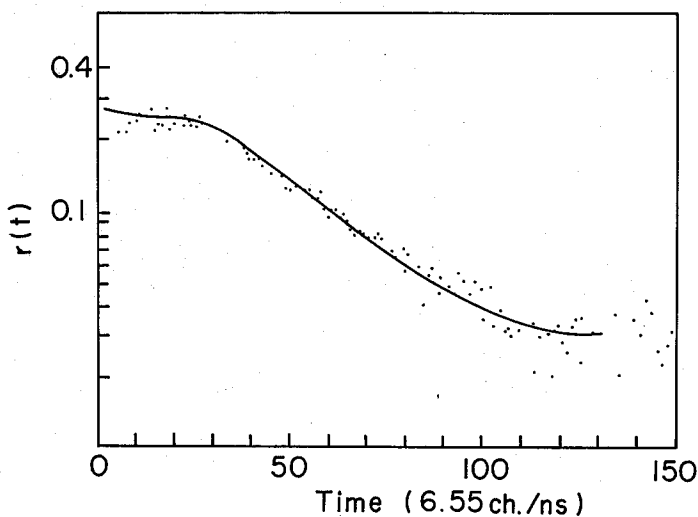


Fig. 4. $r(t)$ vs. time for Pst A1 in cyclohexanone. Dots are the observed values and solid line is the calculated curve.

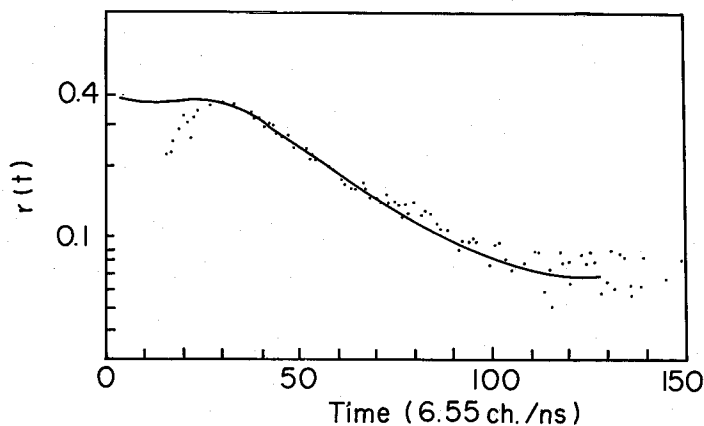


Fig. 5. $r(t)$ vs. time for Pst B1 cyclohexanone. Dots are the observed values and solid line is the calculated curve.

The fact that the observed values could be simulated by the calculated curve implies that in this time resolution the local motion of polystyrene in dilute solution can be expressed by only one relaxation time. As a result of this simulation, the intrinsic anisotropy ratio, r_0 was determined to be 0.26 for the Pst A series and 0.40 for the Pst B series. The anisotropy ratio for similar systems such as polystyrene labeled with 9-phenyl-10-(4-vinylphenyl)anthracene²⁰ or 9-vinylphenylanthracene²¹ has been reported to have two components. The anisotropy ratio $r(t)$ for anthracene probe conjugated just in the middle of polystyrene was well simulated by the generalized diffusion and loss model, where the relaxation time consists of two components.^{10,11} The shape of perylene molecule is highly anisotropic, and a free perylene molecule in solution is expected to show a complicated relaxation course.²² In the present study only one relaxation time in this time range was observed for perylene bound to polystyrene chain. It seems unplausible that the local motion of perylene probe conjugated to polystyrene as a side group is really isotropic. There are several possibilities for this: i) the perylene probe is attached to the polymer chain as a pendant, then the optical axis is perpendicular to the polymer chain and the motion of such a probe looks isotropic in this time resolution, ii) the present time resolution of the apparatus is not enough to resolve the distribution of the relaxation times: fwhm of the pulse is ca. 2.4 ns. For Pst A series, the probe can be located at any position in the polymer chains and the local motion at different positions has different relaxation times. For such a sample we may obtain the averaged relaxation time over the location of the probe if the time resolution is not sufficient. This point is being investigated by an improved instrument which we recently built. The r_0 for the Pst B series is close to the theoretical value. The observed r_0 for the Pst A series, however, was rather low. If there are two perylenes in one polymer, intramolecular energy migration may induce fluorescence depolarization. However, 3-vinylperylene in the feed monomer is low ($< 10^{-4}$) and the perylene number in one polymer chain is < 0.02 . Hence the depolarization due to intramolecular energy migration may be discarded. The cause is not clear at present.

Steady-State Rotational Relaxation Times. In the case that the fluorescence decay is a single exponential whose lifetime is τ , the steady state anisotropy ratio R is given by eq. (5).

$$R^{-1} = R_0^{-1}(1 + 3\tau/\rho) \quad (5)$$

where R_0 is the intrinsic anisotropy ratio.

Fig. 6 shows the molecular weight dependence of the relaxation times of the Pst A and Pst B series in a good solvent benzene at 30°C. The relaxation times of the interior and of the chain ends become constant above $M_n \simeq 2 \times 10^4$. For the same M_n samples the relaxation time of the segments in the interior of the chain is about twice as large as that of the terminal segments under the same condition. North and Soutar²¹ reported that the ratio is six or more times in their study on polystyrene labeled with anthracene derivatives. However, their sample was a copolymer of styrene with 9-vinylanthracene. One should note that the polymerization of 9-vinylanthracene prop-

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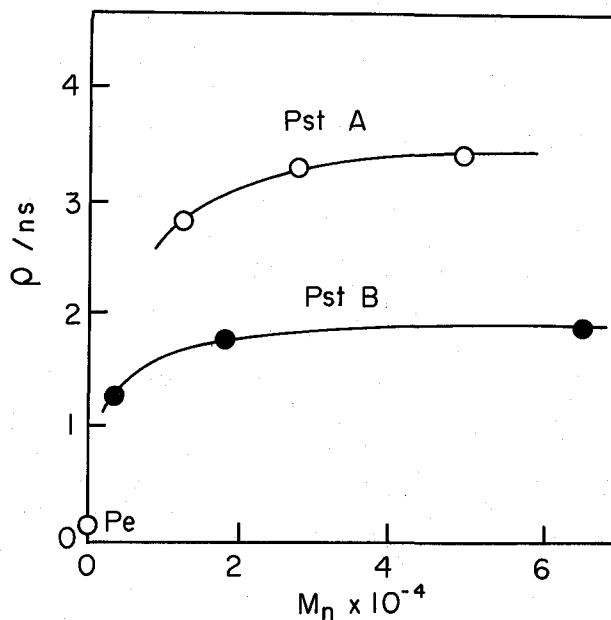


Fig. 6. Molecular weight dependence of the relaxation time ρ in benzene at 30°C.

agates with across-the-ring type dominantly²³⁾ and this structure will give a large value for the relaxation time.

Figs. 7 and 8 show the temperature dependence of the relaxation times for Pst A1 in toluene and cyclohexane solvents. Toluene is a good solvent for polystyrene and

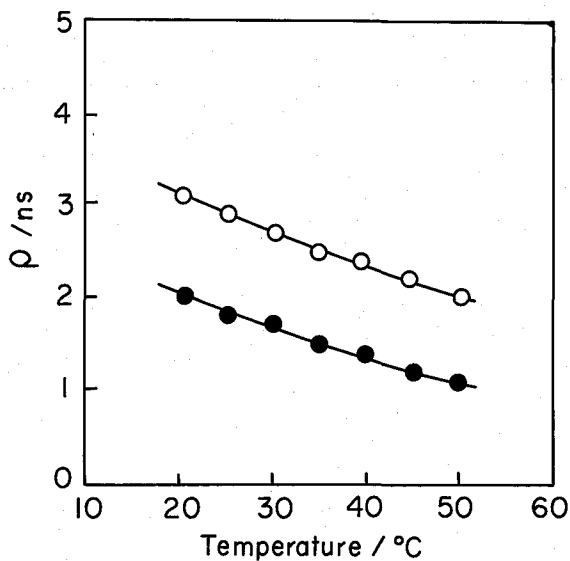


Fig. 7. Temperature dependence of the rotational relaxation time ρ in toluene. The concentration of polystyrene was 0.1 g/dl. The samples were not deaerated.

○: Pst A1, ●: Pst B1

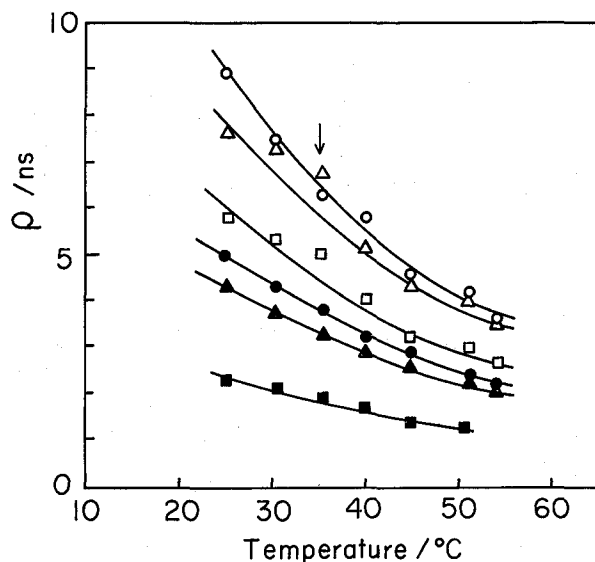


Fig. 8. Temperature dependence of the rotational relaxation time ρ in cyclohexane. The concentration of polystyrene was 0.1 g/dl. The samples were not deaerated.

○: Pst A1, △: Pst A2, □: Pst A3, ●: Pst B1, ▲: Pst B2, ■: Pst B3.

cyclohexane is a theta solvent where the theta temperature is 34.5°C as indicated in the figure. In cyclohexane, no abrupt change of the relaxation time could be observed at the theta temperature. These figures also show that the relaxation times of the interior in the chain is a few times larger than those of the chain ends. Fig. 9 shows Arrhenius plots of ρ/η for Pst A1 sample in toluene and cyclohexane where η is solvent viscosity. Here the relaxation times are scaled by the viscosities of the solvents. The value ρ/η in cyclohexane is much larger than that in toluene. The activation energies of ρ/η were obtained from the slope of ρ/η against $1/T$. The activation energy in cyclohexane is larger than that in toluene. The activation energies in other solvents: cyclohexanone, MEK, benzene are also listed in Table II. The activation energy in cyclohexane is slightly larger than those in other good solvents.

Similar behavior has been reported on polyisoprene in the good and theta solvents by Ediger et al.²⁴⁾ They observed that the local segmental dynamics of polyisoprene in a theta-solvent are slower than those in good solvents and that the apparent activation energy is larger than those in the good solvents. They explained their observations by considering the local segment concentration about the labeled segment. That is, the local segmental concentration around the probe in a theta-solvent is higher than that in the good solvents, then the local motion in the theta-solvent becomes slower. Furthermore, thermal expansion of chain in the vicinity of the theta-point in addition to the activation energy for internal rotational barrier leads to an increased apparent activation energy. In the present systems the activation energies in good solvents are rather small, i.e., smaller than that in the case of diffusion limit (E 2.5 kcal/mol)²⁵⁻²⁷⁾. In such a case, apparent activation energy does not mean true barrier height. Further studies

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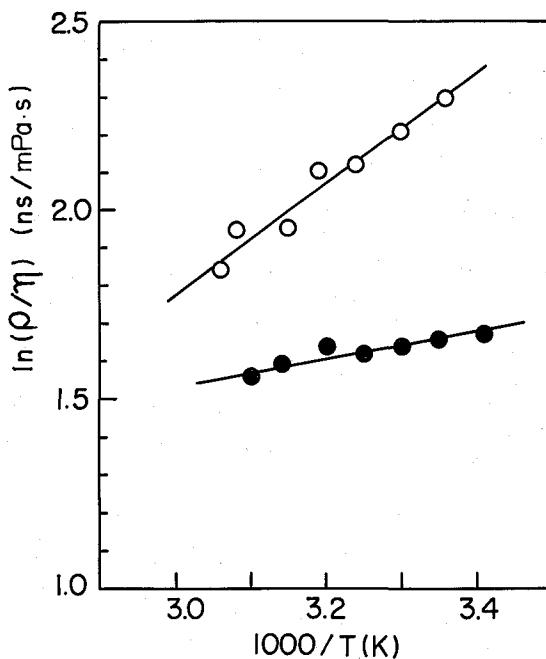


Fig. 9. Temperature dependence of ρ/η in toluene (●) and cyclohexane (○) for Pst A1.

Table II. Activation Energies of ρ/η

Solvent	Pst A1 (kcal/mol)	Pst B1 (kcal/mol)
Cyclohexanone	0.8	1.2
MEK	1.0	1.3
Benzene	0.8	1.3
Toluene	0.8	1.7
Cyclohexane	2.9	2.5

are being undertaken to elucidate temperature dependence of the relaxation times.

CONCLUSION

The results are summarized as follows. (1) The time-resolved anisotropy ratio $r(t)$ of the perylene probe attached in the interiors of polystyrene as a pendant or at the chain ends is roughly represented by a single relaxation time. (2) The relaxation time is 1–10 ns at a temperature between 20 and 60°C. (3) The relaxation time in the interior of the polymer chain is twice as large as that at the chain ends. (4) The apparent activation energy of ρ/η in a theta solvent is slightly larger than those in good solvents. The apparent activation energies in good solvents are slightly smaller than that of diffusion limit.

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